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(54) Process for the production of low substitute, water soluble carboxymethylcellulose

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(57) This patent is for a process for the production of low substitute, water soluble carboxymethylcellulose with DS values less than 0.5, whereby water solubility is already achieved at values less than 0.4, and products having a water insoluble content of approximately 5% or less are obtained. During this process, preactivated cellulose is transferred into an aqueous organic system of very precise, optimal conditions for the contents which include the reacting agents and the liquid components such as water and accompanying mixable organic liquids. According to invention, a mol ratio of the cellulose anhydroglucose unit to the soda lye is established in a range of 1:0.3-0.8 and to the monochloracetic acid in a range of 1:0.3-0.8 with a mass ratio of the cellulose to water of 1:0.5-1.5 and to the organic liquid, for example, ethanol, isopropanol, acetone, of 1:1-10, whereby the water content in the liquid phase is set to between 15 and 35%. In the alkalization step the alkali of the activated cellulose is dissolved in part of the aqueous organic phase in such a way that an alkali concentration between 6% and the saturation concentration, preferably between 9 and 14%, is achieved.

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Title of invention

Process for the production of low substitute, water soluble carboxymethylcellulose

Area of application of invention

This invention is for a process for the production of low substitute, water soluble carboxymethylcellulose, which can serve as a thickener, adhesive or other agent which helps achieve certain desired effects in the textile, paper, food, detergent, dye, chemical and pharmaceutical industries with many other areas of application.

Characteristics of current technical solutions

Currently the sodium salt of the carboxymethylcellulose (CMC) can be obtained by transferring the alkali cellulose with monochloracetic acid into a medium containing water and mixable organic liquids, such as alcholos. According to a process for the production of carboxymethylcellulose as described in DE-OS 1 418 238, the advantage of using such organic liquids is that the cellulose material hardly wells during the transfer and the fibrous-powdery structure of the starting material remains unchanged, with water soluble products being yielded at an average degree of substitution (DS) greater than approximately 0.5. The production of water soluble CMC with DS values less than 0.5 currently requires the use of special very intensive disaggregating devices, or is only possible using a special conversion process, such as the one described in DE-OS 1 568 751. Using this process in a preferred manner, it is necessary to have a large excess of sodium hydroxide in a mol ratio of 2.35 mol per mol unit of the cellulose anhydroglucose in the presence of a large amount of an organic liquid as the diluting agent. After alkalization, the large excess of alkali must be reduced, by adding an acetic acid, for example, back to a level of 1.2-1.5 mol per mol unit of anhydroglucose, so that the subsequent etherization reaction can be carried out to a water soluble product with DS = 0.38 with approximately 0.48 mol monochloracetic acid per mol unit of anhydroglucose. During this process it is necessary to dilute each part of cellulose with 1.2 parts water and a large amount of a low alcohol, 16.2 parts by weight, which greatly restricts the space-time yield.
Furthermore, it is also well-known that treating the cellulose with ammonia causes the cellulose structure to loosen and change considerably because of the conversion from ordered to less ordered areas, as described for example in Faserforschung und Textiltechnik 24 (1973) pp. 371-376. It is also known that such activated cellulose is easily converted in an aqueous reaction medium to soluble cyanethylcellulose in diluted alkali solutions, as described in DD-PS 118 096.

Goal of invention

It is the goal of the invention to develop a process for the production of carboxymethylcellulose which uses fewer chemicals, especially monochloracetic acid and soda lye, and/or with an improved space-time yield compared to other processes and yields products, which are already water soluble with DS values < 0.5 and containing only small amounts of material not soluble in water.

Characteristics of invention

- Problem definition
  The task for the invention is to produce a low substitute, water soluble carboxymethylcellulose with a DS < 0.5 from a preactivated cellulose by alkalization and carboxymethylization in a partially non-aqueous reaction medium.

- Characteristics of the invention
  According to invention the process for the production of soluble carboxymethylcellulose overcomes the shortcomings and disadvantages of the processes currently in use and leads to products with acceptable water solubility DS values which are less than 0.5. In this process, the cellulose is activated, preferably with liquid ammonia, and fermented by a process of carboxymethylization described in the following paragraphs with a comparatively small amount of sodium hydroxide, which lies in the range of 0.7-1.7, preferably 0.85-1.25 mol, in particular double the mol number with respect to the use of monochloracetic acid, plus a small excess of approximately 5 mol % per mol unit of cellulose anhydroglucose. Furthermore, a liquid which can be mixed with water, for example, a low molecular alcohol such as ethanol or isopropanol, or a ketone such as acetone, is added in an amount that will produce a ratio of cellulose to water preferably in the range of 1:0.5-1.5 parts by weight and a ratio of cellulose to organic liquid in the range of 1:1-10, preferably 1:1-4 parts by weight.
  The amount of monochloracetic acid required in the carboxymethylization process should be between 0.3 and 0.8 mol, preferably between 0.4 and 0.6 mol per mol unit of cellulose anhydroglucose, which is dissolved after alkalization in a partial amount of the water and/or organic liquid, and then added in the appropriate way, for example by a spray process. The liquid portion is then proportioned out in such a way so that the soda lye concentration during alkalization is between 6% and the saturation concentration during the liquid phase, preferably between 9% and 11%.
  The carboxymethylization process occurs by a rise in temperature and treatment in a temperature range from 30° to 100°C, preferably from 50° to 70°C, until the monochloracetic acid is almost completely converted in a suitable aggregate unit such as a kneading mixer, for example. According to invention, the process, which uses fewer chemicals compared to current processes, leads to low substitute, water soluble CMC products with DS values less than 0.5 and less than 0.4 when the process is carried out in a more ideal manner. Also, after centrifuging (15 minutes at 2000 g) certain parts which remained undissolved were still minimal resulting in a smaller amount of chemicals being used and higher quality products.

Application examples

Example 1

100 parts by weight of beech sulfite cellulose are treated with liquid ammonia for 30 minutes at -50°C and the ammonia residue is steamed off afterwards.
In a kneading mixer the activated cellulose is blended together with a finely divided mixture of 31 parts by weight soda lye, 62 parts by weight water and 150 parts by weight ethanol (96%) and then alkalized at room temperature for 30 minutes. Next a finely divided solution of 35 parts monochloracetic acid in 38 parts water and 90 parts ethanol is prepared, mixed for 30 minutes, then this mixture is heated to 50°C and converted at this temperature for 7 hours. The reaction product, which is worked up by being washed with aqueous methanol and then dried, has a DS of 0.37 and an undissolved proportion of 3.8%. In a replication experiment, the cellulose which was not activated with ammonia yielded a product with a DS of 0.35 and an undissolved proportion of 12%.

Example 2

100 parts beech sulfite cellulose are activated with liquid ammonia as in the first example above, then alkalized in 12.8% aqueous alcoholic soda lye and mixed with 0.6 mol/mol unit of the cellulose

anhydroglucose using monochloracetic acid. The difference between this process and the one in the first example is that here the mixture is heated to 70°C and carboxymethylized for 4 hours. The purified product has a DS of 0.42 and an undissolved proportion of 5.2%. In a replication experiment, the cellulose which was not activated yielded a product with a DS of 0.45 and an undissolved proportion of 18%.

Patent claims

1. Process for the production of low substitute, water soluble carboxymethylcellulose by converting preactivated cellulose, whereby the alkalization and carboxymethylization occurs in such a manner so that the mol ratio of the unit of cellulose anhydroglucose to sodium hydroxide is in a range between 1:0.7-1.7, preferably 1:0.85-1.25, the mol ratio of the unit of cellulose anhydroglucose to monochloracetic acid is in a range between 1:0.3-0.8, preferably 1:0.4-0.6, the mass ratio of cellulose to water is 1:0.5-1.5 and the mass ratio of cellulose to organic liquid is 1:1-10, preferably 1:1-4, and the water content in the liquid phase is between 15 and 35% and that the alkali is dissolved in a portion of the aqueous organic phase and added to the cellulose in the alkalization step, so that the concentration of sodium hydroxide is between 6% and the saturation concentration, preferably between 9% and 14%.

2. Process according to claim 1, whereby organic liquids which are mixable with water such as low alcohols, preferably ethanol, isopropanol or low ketones, preferably acetone, are used.